Dewatering Process

The present invention concerns the flocculation and dewatering of aqueous suspensions to form a dewatered cake.

It is well known to apply flocculants to aqueous suspensions in order to separate solids from the suspension. For instance it is common practice to flocculate and then dewater suspensions containing either suspended solid organic material or mineral solids. For instance it is common practice to flocculate sludges such as sewage sludge, waste waters, textile industry effluents, red mud from the Bayer Alumina process and suspensions of coal tailings etc. Flocculation is usually achieved by mixing into the suspension the flocculant, allowing the suspended particles to flocculate and then dewatering the flocculated suspension to form a dewatered cake.

In the dewatering of suspensions it is known to add a high molecular weight, water soluble polymer as a flocculant to the suspension in order to remove the liquid from the suspension and greatly increase the dry solids of the suspension. High molecular weight flocculants may be cationic, anionic, nonionic or amphoteric in nature. The choice of polymeric flocculant will largely depend upon the susbstrate, which is being treated. For instance it is common practice to use high molecular weight cationic flocculants to treat aqueous suspensions comprising suspended organic material, for instance sewage sludge. In paper-making it is known to use either cationic, nonionic, anionic or amphoteric flocculants. Flocculation of mineral suspensions is frequently effected by use of anionic flocculants.

It is standard practice to apply polymers as aqueous compositions to flocculate suspensions containing suspended organic material. Generally the compositions of polymers are relatively dilute, for instance no more than 1% and usually no more than 0.5%, and can be as low as 0.2% by weight or lower.

Various alternative methods of introducing a flocculant into a suspension have been proposed. WO-A-02/079099 describes a method in which at least one flocculant emulsion is added directly to a solids liquid separation process and inverted in situ such that flocculant is released directly into the application. The emulsion is added specifically at the solids liquid separation process and subjected to an effective amount of high shear for sufficient time and pressure to ensure rapid inversion of the emulsion in and complete release of the flocculant into the bulk suspension before any initial separation.

WO-A-98/31749 and WO-A-98/31748 are both concerned with preparing dispersions of high intrinsic viscosity cationic polymers in an aqueous and medium containing dissolved low intrinsic viscosity cationic polymer. The product thus formed is an aqueous dispersion of undissolved high intrinsic viscosity cationic polymer which is a convenient way of providing high molecular weight flocculants. The dispersion polymer can be dissolved in water to a conventional concentration or can be added directly to a suspension.

It is also known to use two different polymeric flocculants in the same process. In commercial practice the dewatering of sewage sludge may involve the addition of two polymeric flocculants which have the same charge (co-ionic). In other processes it is known to apply two polymers of opposite charge (counter-ionic). Where two polymeric flocculants are applied to an aqueous suspension they may be added simultaneously or more usually sequentially.

WO-A-01/05712 reveals a process of dewatering a suspension by adding to the suspension a concentrated and a dilute solution of polymeric flocculants substantially simultaneously. Both the concentrated and diluted solutions of polymer are added at conventional concentrations of no more than 1% and usually much less than this.

WO-A-02/72482 describes a process of flocculating and dewatering an aqueous suspension of suspended solids in which a polymer composition comprising 40% and 60% by weight polymer and a polymer composition comprising between 0.05 and 0.2% by weight polymer are introduced simultaneously. Although the process brings about some improvements in filtration and free drainage, it would be desirable to improve upon the cake solids obtained in dewatering suspensions, especially for sewage sludges.

International application PCT/EP03/09381, unpublished at the priority date of the present application, describes a method of dewatering a suspension employing a composition comprising a cationic polymer flocculant and a coagulant in which the coagulant is encapsulated. After free drainage of the suspension the coagulant is released into the suspension for example by rupturing of the capsules which enclose the coagulant or by migration from a matrix in which the coagulant is entrapped. Although significant improvements in cake solids can be obtained it would be desirable to provide equivalent or improved cake solids using flocculant products that can be more easily manufactured and/or applied.

However, achieving high cake solids can sometimes be difficult, particularly in the dewatering of sewage sludges. It is also known to add a flocculant or coagulant to assist the initial dewatering of a suspension followed by further addition of flocculant or coagulant and then further dewatering to achieve high cake solids. Such processes are described in JP-A-10-249398, JP-A-61-257300, JP-A-06-343999, JP-A-06-344000 and EP-A-1035077. However, these processes have the disadvantage that they require two stages of dewatering involving two separate treatments with flocculant.

It would be desirable to provide an improved process that results in dewatering of suspensions to provide increased cake solids. In particular it would be desirable to provide such a process that involves treatment agents that can be

more easily and conveniently manufactured and applied. A further objective of the present invention is to provide a process that avoids the necessity of employing flocculant additions in two separate steps.

According to one aspect of the present invention we provide a process of dewatering an aqueous suspension employing a flocculating system comprising treating the suspension with a flocculating amount of a first flocculant and a dewatering amount of a second flocculant, and subjecting the suspension to mechanical dewatering to form a cake, wherein the first flocculant brings about flocculation and assists thickening of the suspension and the second flocculant further dewaters the suspension,
characterised in that the second flocculant is a water-soluble or water swellable polymer that is mixed into the suspension in the form of an aqueous composition comprising dissolved or hydrated polymer having a Brookfield viscosity of above 30,000 cps (measured at 20°C, RVT viscometer, spindle 6, 1rpm).

The invention is applicable to any suitable suspensions in which it is desirable to concentrate the suspended solids. This includes waste waters, and textile industry effluents, mineral suspensions such as red mud from the Bayer Alumina process or coal tailings, in paper mill wastes such as cellulosic sludges. The process is particularly applicable to the dewatering of sewage sludge.

In the dewatering processes the suspension is first thickened following the addition of the first flocculant. This stage involves the initial flocculation and release of free water to produce the thickened suspension. Generally the release of free water may be achieved by free drainage or filtration and it is common to employ mechanical means such as a belt thickener, belt press rotary drum thickener or centrifuge. The flocculant should be applied in sufficient quantity to bring about initial flocculation and partial dewatering of the suspension. Preferably the suspension is thickened to produce a semi solid

sludge paste. In general this first flocculant will be a polymer added at a conventional concentration, for instance 0.1% to 1% by weight, especially 0.2% to 0.5%.

Typically addition of the first flocculant and second flocculant would be into the initial bulk suspension.

The dewatering processes requires the action of the second flocculant upon this thickened suspension. We find that the relatively viscous second flocculant does not substantially mix into the bulk suspension prior to thickening but it does integrate into the thickened suspension during mixing and/or mechanical dewatering and brings about further release of water to produce a dewatered cake. The second flocculant can be easily mixed into the thickened suspension and distributed throughout using conventional mixing equipment. Suitable mixing equipment includes for instance ribbon type mixers or kneading mixers. Ribbon type mixers consist of helical or spiral mixing blades that sweep across nearly the entire surface of the mixing vessel. Kneading mixers consist of two kneading arms that intermesh as well as form a close tolerance to the mixer wall. Alternatively the second flocculant can be distributed throughout the thickened sludge during mechanical dewatering. Typically, this mechanical dewatering will involve compression and can for instance be any of belt press, filter press, screw press or centrifuge. When this treated thickened suspension is subjected to mechanical dewatering unexpectedly high cake solids can be achieved.

Preferably the second flocculant is an aqueous composition comprising either dissolved and/or hydrated polymer. More preferably the aqueous composition will comprise at least 2% by weight polymer. Generally the polymer concentration would be at least 5% and often at least 10%. The aqueous composition may comprise as much as 20% or more, for instance up to 25 or 30% polymer but generally useful results are obtained when the polymer

concentration is between 5% and 20% by weight. The amount of polymer used in the second flocculant composition will depend upon the type, molecular weight, and degree of crosslinking of the polymer. Generally higher molecular weight polymers can be used in lower concentrations than lower molecular weight polymers. Thus the exact amount of polymer is sufficient to generate a Brookfield viscosity of above 30,000 cps. Usually the second flocculant composition will exhibit a viscosity of at least 40,000 cps and often can be at least 60,000 or 80,000 cps. The composition may be significantly more viscous and still produce useful results, for instance 900,000, 1,000,000 or more. Typically more effective results are realised when the second flocculant has a viscosity between 100,000 and 800,000 cps. Particularly preferred compositions will exhibit a viscosity of between 400,000 cps and 800,000 cps.

The first and second flocculants may be any suitable natural or synthetic polymeric flocculant and typically will be high molecular weight. Natural polymers include for instance cationic starch, anionic starch and chitosan etc. Synthetic polymers include linear, branched and cross-linked polymers of ethylenically unsaturated monomers. The first flocculant may be the same as the second flocculant or alternatively the two flocculants may be different. Usually the polymer of the first flocculant and second flocculant will be of molecular weight in excess of 500,000, usually at least one million and normally 5 million up to 30 million.

The first and second flocculants of the present invention may be cationic, anionic, nonionic or amphoteric in nature. The choice of polymeric flocculant will largely depend upon the susbstrate, which is being treated. For instance it is common practice to use high molecular weight cationic flocculants to treat aqueous suspensions comprising suspended organic material, for instance sewage sludge. In treating paper-mill waste it is known to use either cationic, nonionic, anionic or amphoteric flocculants. Flocculation of mineral suspensions is frequently effected by use of anionic flocculants.

The polymer may be prepared by polymerisation of a water soluble monomer or water soluble monomer blend. By water soluble we mean that the water soluble monomer or water soluble monomer blend has a solubility in water of at least 5g in 100 ml of water. The polymer may be prepared conveniently by any suitable polymerisation process.

When the water soluble polymer is nonionic the polymer may be formed from one or more water soluble ethylenically unsaturated nonionic monomers, for instance acrylamide, methacrylamide, hydroxyethyl acrylate, N-vinylpyrrolidone. Preferably the polymer is formed from acrylamide.

When the water soluble polymer is anionic the polymer is formed from one or more ethylenically unsaturated anionic monomers or a blend of one or more anionic monomers with one or more of the nonionic monomers referred to previously. The anionic monomers are for instance acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid, vinylsulphonic acid, allyl sulphonic acid, 2-acrylamido-2-methylpropane sulphonic acid and salts thereof. A preferred polymer is the copolymer of sodium acrylate with acrylamide.

Preferably the water soluble polymer is cationic and is formed from one or more ethylenically unsaturated cationic monomers optionally with one or more of the nonionic monomers referred to herein. The cationic polymer may also be amphoteric provided that there are predominantly more cationic groups than anionic groups. The cationic monomers include dialkylamino alkyl (meth) acrylates, dialkylamino alkyl (meth) acrylamides, including acid addition and quaternary ammonium salts thereof, diallyl dimethyl ammonium chloride. Preferred cationic monomers include the methyl chloride quaternary ammonium salts of dimethylamino ethyl acrylate and dimethyl aminoethyl methacrylate. A particularly preferred polymer includes the copolymer of acrylamide with the methyl chloride quaternary ammonium salts of dimethylamino ethyl acrylate.

The polymers may be linear in that they have been prepared substantially in the absence of branching or cross-linking agent. Alternatively the polymers can be branched or cross-linked, for example as in EP-A-202780.

Desirably the polymer may be prepared by reverse phase emulsion polymerisation, optionally followed by azeotropic dehydration to form a dispersion of polymer particles in oil. Alternatively the polymer may be provided in the form of beads by reverse phase suspension polymerisation, or as a powder by aqueous solution polymerisation followed by comminution, drying and then grinding. The polymers may be produced as beads by suspension polymerisation or as a water-in-oil emulsion or dispersion by water-in-oil emulsion polymerisation, for example according to a process defined by EP-A-150933, EP-A-102760 or EP-A-126528.

It is particularly preferred that the second flocculant is formed from at least 30% by weight cationic monomer or monomers. Even more preferred are polymers comprising at least 40 or 50% by weight cationic monomer units. It may be desirable to employ cationic polymers having very high cationicities, for instance up to 80 or even 100% cationic monomer units. It is especially preferred when the cationic second flocculant polymer is selected from the group consisting of cationic polyacrylamides, polymers of dialkyl diallyl ammonium chloride, dialkyl amino alkyl (meth) -acrylates (or salts thereof) and dialkyl amino alkyl (meth)-acrylamides (or salts thereof).

As stated previously the second flocculant is desirably of relatively high molecular weight. Normally the second flocculant will be a polymer that exhibits an intrinsic viscosity of at least 0.5 dl/g. Typically the intrinsic viscosity will be at least 3 dl/g, and often it can be as high as 20 or 30 dl/g but preferably will be between 4 and 10 dl/g.

Intrinsic viscosity of polymers may be determined by preparing an aqueous solution of the polymer (0.5-1% w/w) based on the active content of the polymer. 2 g of this 0.5-1% polymer solution is diluted to 100 ml in a volumetric flask with 50 ml of 2M sodium chloride solution that is buffered to pH 7.0 (using 1.56 g sodium dihydrogen phosphate and 32.26 g disodium hydrogen phosphate per litre of deionised water) and the whole is diluted to the 100 ml mark with deionised water. The intrinsic viscosity of the polymers is measured using a Number 1 suspended level viscometer at 25°C in 1M buffered salt solution.

One particularly useful cationic polymer type for use second flocculant includes 50 to 100% by weight methyl chloride quaternary ammonium salt of dimethyl amino ethyl (meth) acrylate and 0 to 50 % by weight acrylamide of intrinsic viscosity between 4 and 10 dl/g. Preferably the cationic polymer comprises at least 80% methyl chloride quaternary ammonium salt of dimethyl amino ethyl (meth) acrylate.

Other suitable polymeric second flocculants include polyvinyl amidine and polyvinyl amines of intrinsic viscosity greater than 1 dl/g, preferably greater than 2 dl/g.

Another particularly suitable category of second flocculants is Mannich addition polyacrylamides. Ideally such polymers will exhibit an intrinsic viscosity greater than 1 dl/g and quite often can be at least 4 dl/g, for instance at least 7 or 8 dl/g. Such polymers may be made by reacting formaldehyde / amine adducts with polyacrylamide. The amine may for instance be dimethylamine or other secondary amines. Preferably the Mannich addition polyacrylamides are quaternised salts and these could be prepared by reacting the free base Mannich with a suitable quaternising agent such as methyl chloride or dimethyl sulfate.

Another suitable polymer as the second flocculant includes poly dimethyl diallyl ammonium chloride of intrinsic viscosity greater than 0.5 dl/g, preferably at least 1 dl/g.

Effective dewatering of suspensions can be achieved when these polymers are used as the second flocculant.

In a further aspect of invention we find that the second flocculant can be used in a number of different processes for dewatering suspensions. The second flocculant may be used alone or with other flocculating systems. It appears that the action of the second flocculant on a thickened suspension, especially a thickened sewage sludge, brings about unexpectedly high release of water and can generate extremely high cake solids, by comparison to conventional processes. Thus according to this further embodiment of invention we provide the use of an aqueous flocculant composition for dewatering an aqueous suspension,
wherein the composition comprises a water-soluble or water swellable polymer which is dissolved or hydrated,
characterised in that the aqueous composition has a Brookfield viscosity of above 30,000 cps (measured at 20°C, RVT viscometer, spindle 6, 1rpm).

Particularly effective results are obtained though when the aqueous composition is used as the second flocculant in conjunction with the first flocculant and according to the first aspect of the invention.

The dose of aqueous composition depends on the substrate and usually this will be a conventional amount. Typically for sewage sludge treatment the dose of the aqueous composition (second flocculant) found to be an effective dewatering amount is often at least 50 mg active polymer per litre of suspension. Usually the amount would be higher for instance up to 400 mg per litre. Preferred doses are between 60 and 300 mg per litre. The quantity of first

flocculant used will usually be at least 50 mg active polymer per litre of suspension and can be as high as 500 or 600 mg per litre. Preferred doses would be between 100 and 400 mg per litre.

Various polymers may be used as the first flocculant in order to obtain a suitably thickened suspension for treatment with the second flocculant. Preferably the first flocculant is a cationic organic polymer. This is particularly true when the suspension is a sewage sludge. Preferred cationic polymers include polymers selected from the group consisting of acrylamide polymers, polyvinyl amidine, polyvinyl amine, poly dimethyl diallyl ammonium chloride, poly amines, polyethyleneimines, mannich polyacrylamides and quaternised mannich polyacrylamides.

The first and second flocculants may be added sequentially and in which case usually the second flocculant is added to the suspension first and although the reverse order may be employed. Normally the first and second flocculants are added in close proximity and preferably they are added substantially simultaneously. When the two flocculants are added in this way they can desirably be added separately although in some situations the first flocculant and the second flocculant are combined into a single composition with beneficial results.

Particularly effective results can be achieved when the first and second flocculants are added to the sludge simultaneously but separately. Without being limited to theory it is believed that the first flocculant results in flocculation of the sludge and the undispersed polymer of the second flocculant becomes trapped within the flocculated structure but does not bring about any significant dewatering until the flocculated sludge is thickened and then by mixing the polymer of the second flocculant is allowed to distribute throughout and integrate with the sludge and achieve further dewatering.

The following example is an illustration of the invention.

Example

Dewatering of aqueous suspensions via a one-stage addition of conventional and high strength organic polymer flocculants

Polymers

Polymer A is a linear, high molecular weight, high cationic acrylamide based polymer of intrinsic viscosity 12 dl/g in the form of a dehydrated emulsion (liquid dispersion product). Polymer B is a linear, low -medium molecular weight, cationic homopolymer of quaternised dimethyl amino ethyl methacrylate of intrinsic viscosity 5 dl/g based polymer in bead form.

Unless otherwise stated intrinsic viscosity is measured using a Number 1 suspended level viscometer, in 1M sodium chloride buffered to pH 7 in accordance with the information given in the description.

Test substrate

Dewatering tests were conducted on a sample of a digested, mixed primary/activated sludge. The sample had a dry solids content of 3.28%.

Experimental procedure

(A) One-stage addition of polymer(s)

i) Polymer A was first dissolved in deionised water to give a homogeneous 1% w/v solution and further diluted to 0.25%w/v prior to use. Polymer B was dissolved in deionised water to give two homogeneous solutions of 1%w/v and 20%w/v. The 1%w/v solution was further diluted with deionised water to 0.25%w/v prior to use.

ii) 250 ml of a digested, mixed primary/activated sludge was placed in a 1 litre plastic beaker (120cm diameter by 120cm tall). A standard laboratory stirrer was secured over the beaker with the stirrer shaft located through a hole in the centre of the beaker lid. The stirrer is a four bladed, flat crosshead type (each paddle is 25cm width by 1.1cm).

iii) The appropriate volume of a 0.25% solution of Polymer A, and a 0.25% or 20% solution of Polymer B, were added simultaneously to the sludge using a syringe and the lid secured to the beaker. The sludge was flocculated by stirring at 1500rpm for 10s. The flocculated sludge was poured into a filtration cell, which had a filter membrane, comprising an 8cm diameter belt-press filter cloth, and the filtrate collected in a measuring cylinder.

iv) After 30s drainage the thickened sludge retained on the filter cloth was subjected to a 'furrowing' technique, whereby a spatula was slowly drawn across the sludge in several directions to encourage release of more water. Furrowing was carried out for 30s. The volume of filtrate was noted.

v) The thickened sludge was transferred to a 250ml beaker and stirred by hand for 45s with a spatula, using a slow, circular folding action.

vi) The thickened sludge was then transferred to a piston-press device and subjected to a compression dewatering stage. Dewatering was commenced using a pressure of 20psi for 2 minutes, followed by increases of 10psi, at one minute intervals, for a further 3 minutes to a maximum of 60psi. Pressure was maintained at 60psi for a further 5 minutes, giving a total compression dewatering time of 10 minutes. The wet cake was removed and the cake solids content was determined by heating at 110°C overnight.

(B) One-stage addition of polymer(s) excluding mixing of the thickened sludge.

The procedure was exactly the same as that described in Section (A) except:

Section v) was omitted

(C) Control – Addition of high strength solution polymer in a two-stage process

The procedure was as that given in Section (A) except:

Section iii) – the appropriate volume of a 0.25% solution of Polymer A was added to the sludge using a syringe and the lid secured to the beaker. The sludge was flocculated by stirring at 1500rpm for 10s. The flocculated sludge was poured into a filtration cell comprising an 8cm diameter belt-press filter cloth and the filtrate collected in a measuring cylinder.

Section v) - the thickened sludge was transferred to a 250ml beaker. The appropriate volume of a 20% solution of Polymer B was added using a syringe into the thickened sludge. To mix in the polymer the treated thickened sludge was stirred by hand for 45s with a spatula, using a slow, circular folding action.

Results

The results are given in Table 1

Table 1

Data Set	Test Procedure	Polymer A Dose (mg/l)	Filtrate Volume (ml)	Polymer B		Cake solids(%)
				Dose(mg/l)	Solution strength(w/v)	
1	A	200	160	100	0.25%	14.73
		200	158	150	0.25%	15.60
		200	156	200	0.25%	15.92
2	B	200	161	100	0.25%	16.07
		200	156	150	0.25%	16.86
		200	156	200	0.25%	17.60
3	A	200	-	75	20%	19.58
		200	164	100	20%	20.72
		200	160	150	20%	21.99
4	C	200	156	75	20%	20.26
		200	-	100	20%	21.42
		200	-	150	20%	21.64

Data set 1 and 2 represent conventional addition of dilute polymer solutions to sewage sludge. The results show that, with conventional treatment, additional mixing of the thickened sludge (Set1) has an adverse effect on cake solids compared to no additional mixing (Set 2).

Data Sets 3 and 4 show that improved cake solids can be achieved by adding a high strength solution at the first stage (Set 3) and that this is just as effective as adding a high strength solution at the second stage (Set 4).